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Preparation of liquid polyesterpolyols from glucose and its methyl derivative

Received: August 6, 2003 / Accepted: October 14, 2003

Abstract Preparation of liquid polyols from D-(+)-glucose (Glc) and its derivative, methyl- α -D-glucoside (m-Glc), has been studied. Direct reaction of ϵ -caprolactone (CL) with Glc (CL:Glc = 2:1–5:1 in weight ratio) at 150°C using tin(II) 2-ethyl hexanoate (SnEht₂) (series A), in which melted Glc was suspended in CL, resulted in a dark-brown coloration of the reactants. The reaction was accompanied by formation of high molecular weight resins, a pH drop, production of water, and a considerable decrease in the hydroxyl value from the theoretically expected one. In the case of Glc/ethylene glycol (EG)/CL reaction system with SnEht₂ catalyst at 150°C (series B), in which the weight ratio of Glc to EG was fixed at 1:1, Glc dissolved in the EG/CL mixture, but the brown coloration of the reactant mixture still occurred. In this case, the formation of water was enhanced, but the other effects found in series A were suppressed to a considerable extent. In the m-Glc/CL/SnEht₂ reaction system (series C), in which m-Glc reacted with two to five times weight amounts of CL under the same conditions adopted in series A, development of the color, the production of high molecular weight materials and water, and the changes in pH and hydroxyl value were not observed. These results are discussed based on the chemical structural differences: Glc exists mostly in the hemiacetal form, but tautomerizes to the aldehyde, whereas m-Glc is an acetal and is protected from reversion to the aldehyde.

Key words Liquid polyol · D-(+)-Glucose · Methyl- α -D-glucoside · ϵ -Caprolactone · Ethylene glycol · Polyurethane foam

Introduction

Interest in and demand for converting biomass into industrially producible materials and/or energy sources has increased in recent years. In accordance with this trend, the material conversions of wood, cellulose, starch, and other abundant biomass into thermoplastic or thermosetting resins, a composite materials with good mechanical performance, and specific functional materials in combination with various synthetic compounds, have been extensively studied so far.^{1,2} These applications fall into a major class of material conversions, in which biomass are rendered to maintain their high molecular weight during processing as much as possible.

Another way of biomass utilization is the decomposition to repeating units or low molecular weight compounds by hydrolysis, pyrolysis and so forth, followed by further conversion into value-added materials. However, the attainable efficiency of biomass utilization is usually small. This means that the weight ratio of by-product(s) to the desired product (E factor)³ is large. For instance, in the case of ethanol production, the yield for the hydrolysis of cellulose with dilute sulfuric acid into glucose is generally as low as 50%,⁴ even though a high temperature of 220°C was adopted for the treatment, and that for successive fermentation (enzymatic) of glucose to ethanol is stoichiometrically 51% ($C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$). Production of CO and H₂ by incomplete burning of biomass, from which methanol can be induced, also occurs in low yield (ca. 50%).⁵ Direct liquefaction (oilification) of biomass into hydrocarbon-like liquid materials, by treatment at high temperatures (300–400°C) with or without synthetic gases, organic solvents (e.g., recycle oils, acetone), catalysts (e.g., Ni, Pd/charcoal, alkali metallic salts) and so forth, usually gives a yield of 23%–60%.⁶

Under these situations, utilization of biomass with a higher atom efficiency⁷ is considered to have some promising values from the point of view of green chemistry. Chemical conversions of sugars or oligosaccharides into their derivatives exhibiting polyol functionality, biodegrad-

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ability or others, are part of this aim. Conversions without any side reactions are particularly desirable. In the present article, as an example of developing biomass into new materials, the chemical conversions of glucose and a related derivative into functional polyols are described.

Materials and methods

Materials

Glucose (Glc) and methyl- α -D-glucoside (m-Glc) were purchased from Nakalai Tesque. Chemicals for synthesis of polyols and for measurement of their molecular weights and distributions and hydroxyl values included ϵ -caprolactone (CL) (Placel M; Daicel Chemical), dimethylsulfoxide (DMSO) and tin (II) 2-ethylhexanoate (SnEht₂) (Wako), and other reagents (Nacalai Tesque). To determine the content of water as a possible coproduct, Hydranal-methanol water standard 5.00 was purchased from Sigma-Aldrich, Japan, and Hydranal Composite 5 and Karl Fischer dehydrate solvent for titration (standard use) were purchased from Hayashi Pure Chemical.

Chemicals for polyurethane foaming included polymeric diphenyl methane diisocyanate (MDI, Nippon Polyurethane), catalyst (*n*-dibutyl-tin-dilaurate, DBTDL), surfactant (SH193; Dow Corning Toray Silicone), and foaming agent (distilled water).

Among the above reagents, CL monomer was purified by vacuum distillation before use, but others were used as received.

Methods

Synthesis of polyols

The outline of the present experiment is shown in Fig. 1. Glc (in series A) or m-Glc (in series C), vacuum-dried at 60°C for more than 12h, was weighed in a flask. In an additional series of experiment (series B), Glc and ethylene glycol (EG) were used in equal proportions on a weight basis. The desired amount of CL was added to each flask, and the respective mixtures were allowed to stand at 150°C under a dry nitrogen stream for 30min, followed by addition of a

small amount (0.33%) of SnEht₂ to act as a catalyst for the ring-opening polymerization of CL. The conditions of the polymerization leading to production of polyols are summarized in Table 1. The experiments, designated as series A, B, and C, were done comparatively. In each series, the reaction was accomplished in two ways, denoted as, for example, A1 and A2 in which the number 1 corresponds to a Glc/CL weight-ratio of 1:2 and the number 2 to a ratio of 1:5.

For characterization of reaction products, the pH, hydroxyl values, water content, and the molecular weight and its distribution were measured. The products obtained may be usable as polyols for polyurethane formulations (described below), surface-active agents, and other similar materials.

Gel permeation chromatography (GPC) analysis

GPC analyses were carried out for synthesized polyols. Molecular weight distributions of the respective samples were determined on a gel permeation chromatograph GPC-900 equipped with a refractive index (RI) detector (Jasco, Tokyo) using TSK-gel G 2000H_{HR} and G 1000H_{HR} columns (Tosoh, Tokyo) connected in series. Measurements were

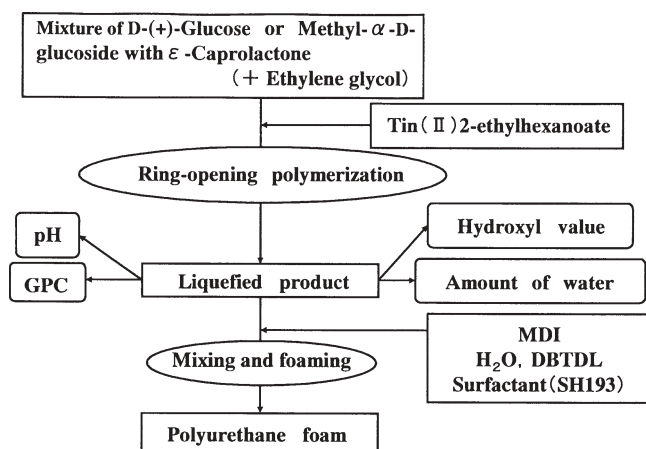


Fig. 1. Flowchart for the experiments. GPC, gel permeation chromatography; MDI, polymeric diphenyl methane diisocyanate; DBTDL, *n*-dibutyl-tin-dilaurate

Table 1. Formulations of chemicals in weight parts for synthesis of polyols

Series	Code	D-(+)-Glucose (Glc)	Methyl- α -D-glucoside (m-Glc)	Ethylene glycol (EG)	ϵ -Caprolactone (CL)	SnEht ₂
A	A1	100	–	–	200	0.990
	A2	100	–	–	500	1.98
B	B1	100	–	100	200	1.32
	B2	100	–	100	500	2.31
C	C1	–	100	–	200	0.990
	C2	–	100	–	500	1.98

Reaction temperature, 150°C; reaction time, 10–150 min; catalyst and its amount: SnEht₂, 0.33% per total of reactant amount (w/w)

conducted by using DMSO as the mobile phase at a flow rate of 0.5 ml/min. The concentration of each sample was 0.5 wt% in DMSO and the injected amount was 100 μ l. The system was calibrated by monodisperse polyethylene oxide standards.

Hydroxyl value determination

To characterize polyol products and determine the amount of diisocyanate required for the preparation of urethane foams from the polyols, their hydroxyl values were measured. The method of the determination was as follows. A polyol sample (1.0 g) was weighed into a 200-ml beaker and a phthalating agent (25 ml) was added. The phthalating agent was prepared in the following way: phthalic acid anhydride (150 g) was dissolved in 1 l of dioxane, into which imidazole (24.2 g) was added and dissolved.

The beaker containing the polyol sample and phthalating agent was placed on a hot plate (110°–130°C), covered loosely with a cling film so that the center became concave, and the contents boiled for 20 min. During this period, the phthalating reaction was completed. After cooling to room temperature, 50 ml of dioxane and 25 ml of deionized water were added to the beaker and stirred vigorously. After the contents were completely dissolved, the remaining carboxyl groups were titrated with a potentiometric titration apparatus (AT-510, Kyoto Electronics). The hydroxyl value was calculated from the following equation.

$$\text{Hydroxyl value (mg KOH/g)} = [(B - A) \cdot f \cdot 56.1] / W$$

where A is the titer of the sample (ml), B is the blank titer (ml), f is a factor of 1 N sodium hydroxide aqueous solution, and W is the mass of the sample (g).

Water content determination

The water content of the polyols prepared was measured by use of the Karl-Fischer Moisture Titrator MKA-510 (Kyoto Electronics). Measurements were conducted in duplicate and the average is reported.

pH determination

pH values of the polyols were measured with a pH meter D-12 (Horiba, Kyoto).

Foam production process

Weighed amounts of polyol, catalyst (*n*-dibutyl-tin-dilaurate), and surfactant SH193 (2.9%, based on the weight of polyol) were mixed well in a paper cup. The polyols synthesized as codes A2 and C2 were used for the preparation. A prescribed amount of MDI was added to the mixture (isocyanate index = 110), which was then stirred with a high-speed agitator (15000 rpm) for 15 s. After stirring, the mixture was moved away from the stirrer to allow creaming and rising of the foam to take place.

Finally, the foam samples were cured at room temperature for more than 24 h. The isocyanate index was calculated as follows:

Isocyanate index =

$$\left[(M_{\text{MDI}} \times W_{\text{MDI}}) / (M_{\text{polyol}} \times W_{\text{polyol}} + M_w \times W_w) \right] \times 100$$

where M_{MDI} is the number of moles of isocyanate groups per gram of MDI, W_{MDI} is the weight of MDI used (g), M_{polyol} and M_w are the numbers of moles of hydroxyl groups per gram of the polyol and water, respectively, and W_{polyol} and W_w are the weight of the polyol (g) and the weight of water in the foam formulation (g), respectively.

Results and discussion

Synthesis of polyols

In series A, irrespective of the weight ratio of Glc to CL, two mutually separated phases were present in the reactant mixture, even after vigorous stirring at 150°C for 30 min, i.e., the mixture was composed of a translucent CL phase (upper) and a cloudy melted Glc phase (lower). Thus, Glc never dissolved in CL. Just after addition of the catalyst SnEht₂, the lower phase became brown. Up to 30 min after the catalyst addition, the two-phase separation could be detected in places, and a considerable increase in viscosity was noted in the lower phase. Further continuation of the reaction with vigorous stirring at 150°C resulted in disappearance of the phase separation, enhanced coloration, and the production of an appreciable quantity of water as by-product. Thus, it was suggested that in series A Glc underwent considerable degradation.

In order to overcome the disadvantage of Glc degradation, an attempt was made to improve the poor compatibility with CL by the addition of EG in the experiments of series B. Glc dissolved readily in EG and this homogeneous liquid state was not impaired by the further addition of CL. Brown coloration was inevitable, however, which proceeded with reaction time, although the degree of color development was lower than the case in series A. Thus, the addition of EG was recognized as still being insufficient, although the added EG was expected to act as an acetalizing agent for Glc to form ethylene glycol- α , β -D-glucoside⁸ to a substantial degree.

To confirm chemical blocking of the C₁ anomeric position in Glc, m-Glc was used in place of Glc in the experiments of series C. Stability of the starting materials under the reaction conditions is an important factor for oligoesterification. Glc exists mostly as the hemiacetal, a hydroxyl cyclic ether, but tautomerizes to the aldehyde form. Aldehydes undergo several condensations to mostly intractable products. m-Glc is an acetal and is protected against reversion to the aldehyde. In series C, m-Glc did not dissolve but was suspended in CL under the same reaction conditions as that described for series A. Figure 2 shows the visual appearances of two polyols obtained by reactions

Fig. 2. Visual appearance of polyols obtained from **a** Glc (series A2) and **b** m-Glc (series C2). **a** Glc/ ϵ -caprolactone (CL) = 1/5 (w/w); catalyst, SnEht₂; reaction temperature, 150°C; reaction time, 150 min; **b** m-Glc/CL = 1/5 (w/w); catalyst, SnEht₂; reaction temperature, 150°C; reaction time, 150 min

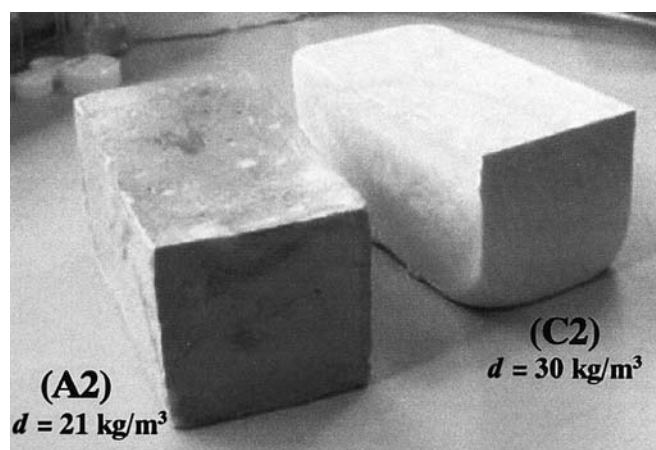
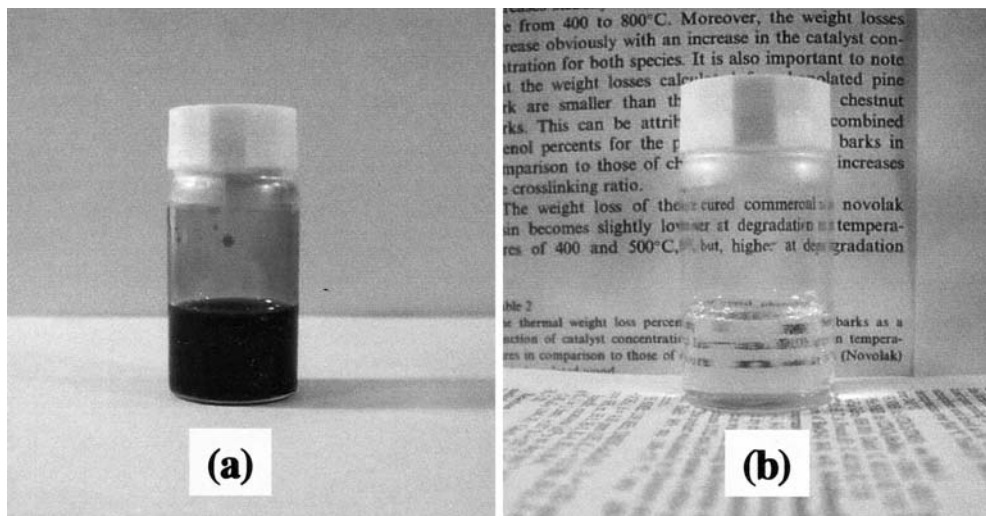


Fig. 3. Visual appearance of polyurethane foams prepared from the glucose polyol A2 (left) and the methyl- α -D-glucoside polyol C2 (right)

using Glc (A2) and m-Glc (C2) as the substrate materials, in which both weight ratios of monosaccharide to CL were 1:5 and the reaction temperature and duration were 150°C and 150 min, respectively. When Glc was the starting material, the mixture became deep brown within ~60 min of the reaction initiation, and was accompanied by a marked increase in the viscosity. On the other hand, when m-Glc was used, the product showed slight yellow coloration but assumed a transparent state (Fig. 2b). Actually, the pale coloration appeared immediately after the start of the reaction, but did not advance further. No significant increase in the viscosity of the reactants was observed in series C, which is in contrast to the former case (series A) using Glc.

Comparison of foams prepared from polyols between series A and C

Figure 3 shows photographs of polyurethane foams that were prepared from the two different polyols shown in Fig.

2. Both foams are of rigid type. The foam prepared from the Glc-derived polyol (A2) had a strong smell of MDI even 3 days after preparation, and contracted considerably, which indicates incomplete formation of polyurethane. In the preparation of polyurethane using the polyol derived from m-Glc, the resulting foam was whitened and never imparted any odor or shrinking behavior. From these results, it can be concluded that the polyols prepared from m-Glc are preferable for fabrication of polyurethane foams.

As has been stated above, when Glc was used as the starting material for polyol synthesis, a strong color change occurred in the ring-opening polymerization of CL at 150°C within a relatively short time. This may be ascribed to surplus denaturation of Glc during the reaction. In the following discussions, possible side-reactions that may cause the degradation of Glc will be taken into consideration.

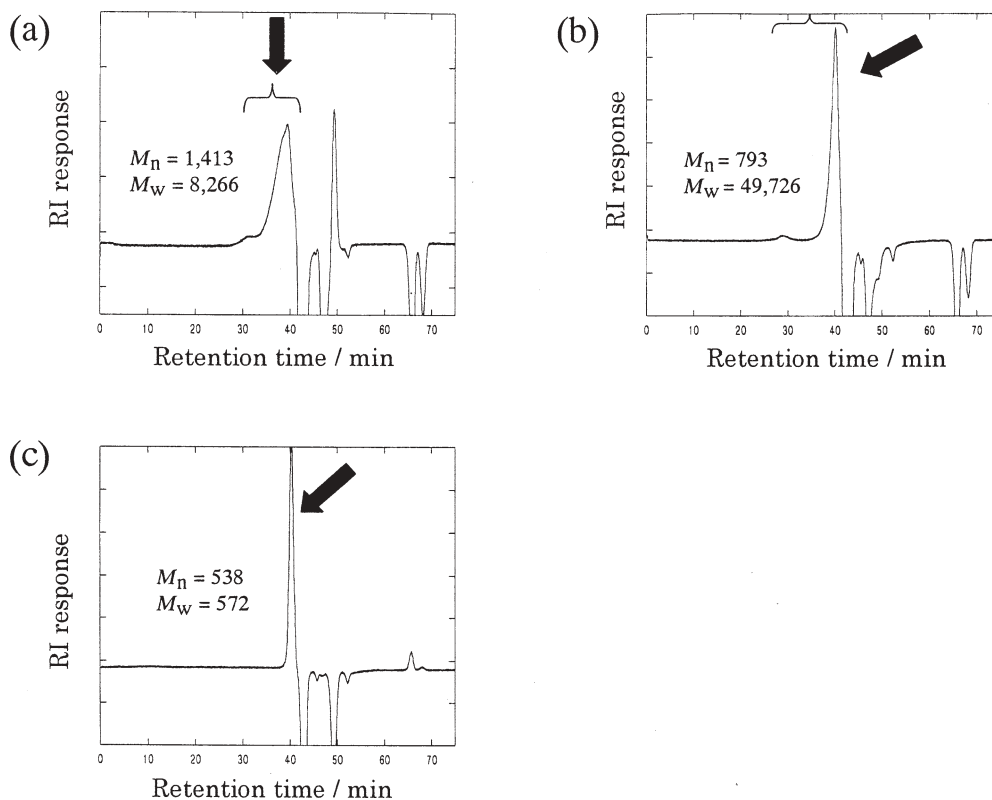
Characterization of reactions in polyol synthesis

For the respective products obtained in the three series of reactions A–C, characterization was conducted through the measurements of molecular weight distributions, pH, water contents, and hydroxyl values, and the difference in mechanism between the three reactions was clarified.

Molecular weight distribution of products

Figure 4 shows molecular weight distribution data obtained by GPC for the reaction products. A peak appearing at a retention time of 35–40 min can be ascribed to the respective major products, which should be polyols derived from Glc or m-Glc combined with oligopolyester chains having a certain distribution of molar substitution (MS) as a result of the ring-opening polymerization of CL. In the GPC data for series A (Fig. 4a), an additional peak appears in the high molecular weight region (retention time <35 min), implying the formation of some side-reaction product. In series B (Fig. 4b), similar production of such high molecular weight

Fig. 4. Molecular weight distribution curves for polyols (indicated by arrows) obtained from **a** Glc/CL (1/5 by weight), **b** Glc/EG/CL (1/1/5 by weight), and **c** m-Glc/CL (1/5 by weight). Synthesis condition: catalyst, SnEht₂; reaction temperature, 150°C; reaction time, 150 min



products is observed but the amount is smaller compared with that in series A. On the other hand, side-products with high molecular weight are not found in series C, as can be seen from Fig. 4c.

In the case in which the reaction period was much shorter than 150 min, a downward GPC peak for residual CL monomer appeared at a retention time of ~47 min; however, it became suppressed with the progress of the reaction and was negligible when the reaction time reached 150 min, as evidenced in Fig. 4. This means that all the CL in the reaction system was consumed by the ring-opening polymerization in the reaction time of 150 min.

pH changes of reactant

The pH values observed after 150 min for the respective reaction mixtures of series A–C are shown in Fig. 5. In series A, the pH became acidic during the polymerization of CL on Glc in the presence of SnEht₂ at 150°C. Addition of EG to the above reaction system depressed the downward pH change, but the phenomenon could still be observed (series B). Usage of m-Glc in place of Glc prevented the pH decline (series C). The result can be explained as follows.

As described above, aldohexoses exist mostly as hemiacetals, a hydroxyl cyclic ether, but tautomerize to the aldehyde form. The aldehyde can be easily oxidized, in the case of Glc producing gluconic acid. The monocarboxylic acid is liable to undergo a dehydration reaction at high temperatures, in which water is eliminated, resulting in hydroxymethyl furfural (HMF). Upon further heating, HMF

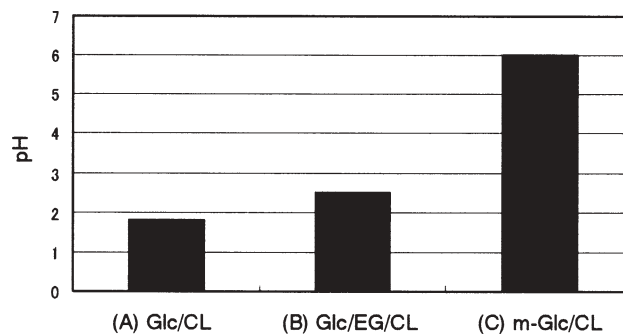


Fig. 5. pH values for the reaction series A–C for synthesizing polyols at 150 and for 150°C min with SnEht₂ as a catalyst. Reactant composition: (A) Glc/CL = 1/2; (B) Glc/EG/CL = 1/1/2; (C) m-Glc/CL = 1/2 (by weight)

decomposes to formic acid, levulinic acid, acetic acid, and other products. Accordingly, in series A, the lowering of pH is inevitable.

On the contrary, m-Glc does not show such decompositions because it remains as a stable acetal with a cyclic pyranose structure. In the case of series B, the decomposition of Glc can occur, although acetal formation of Glc by the action of coexisting EG^{8–12} occurs preferentially and reduces further decomposition of Glc.

Yield of water during reaction

In order to obtain evidence for the above considerations, the amount of water derived from the polyol preparations

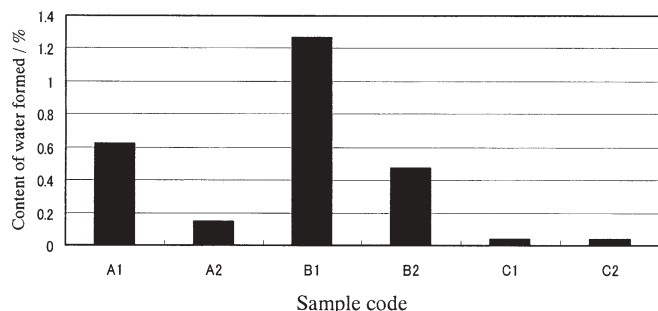


Fig. 6. Amount of water formed in the respective polyol syntheses at 150°C for 90 min. See Table 1 for a description of the sample code A1–C2

was measured by Karl-Fischer titration. The data obtained after 90 min of reaction are compiled in Fig. 6 for the three series. Because water was thoroughly removed by drying and distillation before starting the respective reactions, the measured content of water is taken as that produced in the net reactions.

As shown in the Fig. 6, the reaction of series B formed the highest yield of water, followed by that of series A. Series C yielded negligible water. When comparing the code 1 and 2 reactions in series A and B, it can be pointed out that the yields of water based on the total amount of reactants is larger for code 1 than for code 2. Judging from the fact that the proportion of Glc in the reactants of code 1 was approximately twice that for code 2, the water formation can be attributed to the reaction in which Glc is mainly involved.

The coproduction of water in series A is considered to be due to chemical degradation of Glc, as was described above. The chemical degradation is repressed to some degree by addition of EG in series B, in which EG plays a role of a protective agent against the degradation of Glc.^{8–12} Actually, the presence of EG in the acidic medium at 150°C would cause partial but substantial acetalization at the C₁ anomeric position of Glc, a process in which EG acts as a so-called aglycone. This process yields ethylene glycol- α , β -D-glycoside,^{8–12} eliminating one water molecule for each formation, and, at the same time, prevents Glc from undergoing the dehydration leading to HMF.^{8–11} The considerable extent of water formation in series B suggests the occurrence of substantial acetalization.

Change in the hydroxyl value of reactants

The points raised in the previous discussion can be confirmed by measuring the hydroxyl value of each reactant. Figure 7 shows the relative changes in hydroxyl values with reaction time for each series and code, where the hydroxyl value before starting the respective reactions was taken as 100%. In the case where only the ring-opening polymerization of CL occurs, the hydroxyl value does not change at all during the process. It can be seen from Fig. 7 that the experiments C1 and C2 correspond to this case. In the other cases of series A and B, the decrease in the hydroxyl value is evident and the degree of the lowering is much more severe in series A than in series B. This difference in hy-

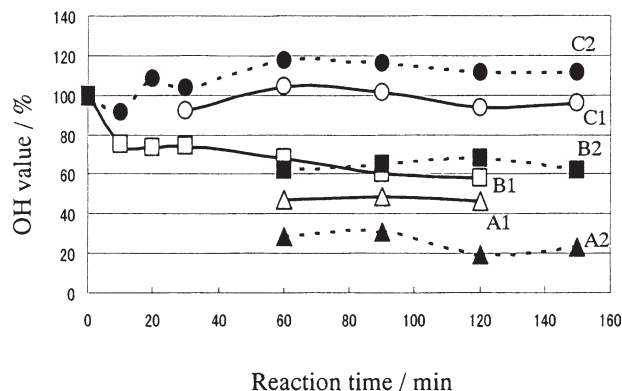


Fig. 7. Reaction-time dependence of the hydroxyl value for the polyol syntheses A1–C2 at 150°C

droxyl value between the two reaction series A and B can be interpreted as follows: a serious extent of dehydration, and the formation of certain amounts of high molecular weight substances, probably obtained from HMF, take place in series A, whereas, in series B, acetal formation of Glc with coexisting EG mainly occurs. Resinification of HMF, in the presence of gluconic acid and other acid products, would reduce the measurable hydroxyl value of the reactant.^{8–11} The plots for B1 cover a wide range of the reaction time, and it is found from the data that there is a relatively sharp decrease in the hydroxyl value for reaction times shorter than 20 min, after which the decreasing rate becomes moderated. This trend is in accordance with the observation of the time course of coloration behavior for the reactant solution.

Conclusions

Preparation of liquid polyols from Glc and m-Glc has been studied. The reaction of Glc with two or five times the mass of CL was carried out at 150°C (series A). In the case of the Glc/EG/CL reaction system (series B), Glc completely dissolved in the EG/CL solution, although the brown coloration as observed in the case of series A also occurred. However, such development of color was suppressed in the m-Glc/CL reaction system (series C).

The products from these three series of reactions were analyzed for the molecular weight distribution by GPC, hydroxyl values, and pH values, and the results were mutually compared. The formation of high molecular weight substances, substantial change in pH toward the acidic range, formation of water, and appreciable decrease in the hydroxyl value were observed for series A. In series B, formation of water was enhanced and the other phenomena found in series A were depressed. In contrast, these phenomena were scarcely observed in series C.

The above results may be explained by the following points:

1. Glc exists mostly as a hemiacetal, a hydroxyl cyclic ether, but tautomerizes to the aldehyde form. It is easily oxi-

dized to gluconic acid, and dehydration also occurs under acidic conditions at high temperature, by which water is eliminated to give HMF. Upon further heating, HMF decomposes to formic acid, levulinic acid, acetic acid, and others. Accordingly, it can be presumed for series A that some high molecular weight substances are formed by polymerization of HMF, attended by the lowering of pH, formation of a considerable quantity of water, and a drop in the hydroxyl values.

2. m-Glc does not decompose like Glc, because the former usually remains as a stabilized acetal with a cyclic pyranose structure.
3. In series B, the decomposition of Glc and, at the same time, acetal formation of Glc by the action of coexisting EG occurs. This should inhibit, to some extent, the decomposition of Glc and therefore formation of further decomposed products.

The internal and macroscopic properties of polyurethane foams obtained from the polyols shown above were also variable, depending on the reaction series for polyol synthesis, as was demonstrated by the comparison between the foams derived from the polyol products A2 and C2.

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